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An octupolar near-IR dye with triphenylamine donors: preparation and absorption properties

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Warmly dedicated to Professor Victor Snieckus on his 65th birthday

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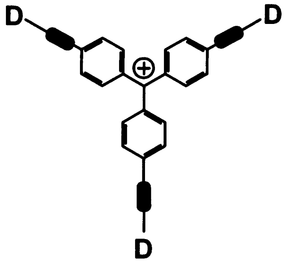
Abstract—A topologically new NIR dye based on a carbocation centered octupole and conjugated triphenylamine donors is described. The dye produced an absorption maximum at 954 nm and by virtue of its two degenerate NBMO–LUMO transitions, showed a large molar extinction coefficient (log ε 4.9). © 2002 Published by Elsevier Science Ltd.

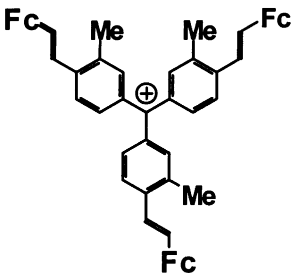
Near-infrared (NIR) absorbing dyes (λ_{max} >700 nm) are of much current interest because of their potential applications in xerography, infrared photography, optical lasers, biological probes, etc.[1] Conceptually, an NIR dye can be prepared by end-capping of conjugated organic chromophores with strong donor and acceptor groups which leads to considerable lowering of the energy of their charge transfer transitions. Most of the NIR dyes that are known today are based on this linear dipolar strategy and consist of extended conjugated backbones, often in the form of long polyene chains, that are end-capped with heterocyclic units acting as the donor/acceptor substitutents. However, as a consequence, these dyes always have large, complex architectures. For example, in NIR polymethine dyes, a polyene chain of at least eight methine carbons is required to produce absorptions beyond 800 nm.[1c] Their structural complexities require multistep syntheses resulting in poor overall yields. Moreover, they are often found to be insoluble in common organic solvents causing difficulties in their purification and applications. In view of these problems, there is a sustained interest in new NIR dyes that are easy to prepare and have strong absorptions (log ε $\geq$5) at longer wavelengths.

Recently, we described a new structural design **A** for the synthesis of NIR dyes.[2] The design consists of an extended octupole in which three donor (**D**) substituted conjugated arms converge on a central carbocation. The octupolar arrangement allows intramolecular electronic interactions to take place between the transition moments of the individual chromophores (excitonic couplings),[3] whereas a strong acceptor center in the form of a carbocation promotes effective mixing of the ground state with the lowest energy excited states. The combined effect gives rise to a low energy transition with increased oscillator strength even when the individual chromophores (dipoles) are relatively small. Using ferrocene as the donor and vinyl groups as the conjugated spacers, we have shown that such an octupolar arrangement can give rise to an organometallic NIR dye **1** with a strong absorption at 1068 nm.[2] Based on this principle, we now describe a new organic NIR dye **6** comprised of triphenylamine donors and vinylene spacers.



A

D = Donor group
▬= Conjugated linker



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(λ_{max} 1068 nm)

Keywords: near-IR dye; octupole; excitonic coupling; triphenylamine; Heck reaction.

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We planned to generate the central carbocation of our octupolar dye through protonation of the corresponding 3° carbinol.[4] Triphenylamine, a weakly basic amine, was chosen as the donor group so that its basicity would not interfere with the protonation of the 3° carbinol. In the event, we started with the commercially available New Fuchsin **2** which via threefold diazotization (dil. H_2SO_4, $NaNO_2$, 0°C) followed by Sandmeyer reaction (KI, H_2O, rt) produced the triiodoaryl carbinol **3** in 40% yield (Scheme 1).[5] A threefold Heck reaction on **3** with 4-vinyltriphenylamine **4** (prepared via a Wittig reaction between 4-formyl triphenylamine with $Ph_3P{=}CH_2$) under Jeffery's phase transfer conditions (cat. $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 100°C)[6] then produced the dye base **5** (60%) after purification by silica gel chromatography.[7] It must be mentioned that an all *trans*-geometry for the vinylene spacers is a vital requirement for our extended octupolar design so as to achieve a large and uniform bathochromic shift (vinylene red shift amounts to ~100 nm). Hence we have used the Heck reaction,[8] known for its high *trans*-selectivity, to construct the vinylene spacers in the dye precursor **5**. The ^1H NMR spectrum of **5** showed a high coupling constant (16.2 Hz) for the vinylene protons confirming their *trans*-geometry. The UV–vis absorption and emission spectra of **5** are shown in Fig. 1. The absorption maximum of **5** was found at 378 nm with a high molar absorptivity (ε_{max} 7.12×10^4 M^{-1} cm^{-1}). Interestingly, the absorption maximum is slightly

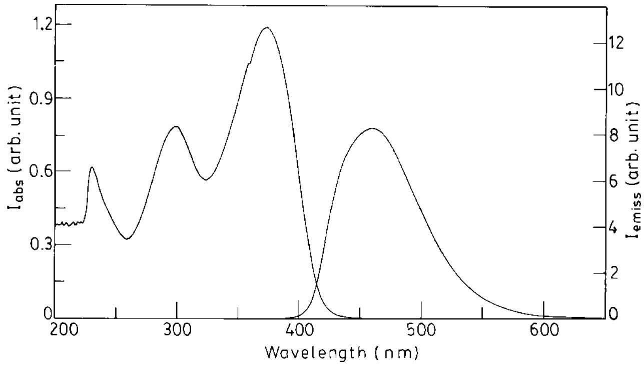
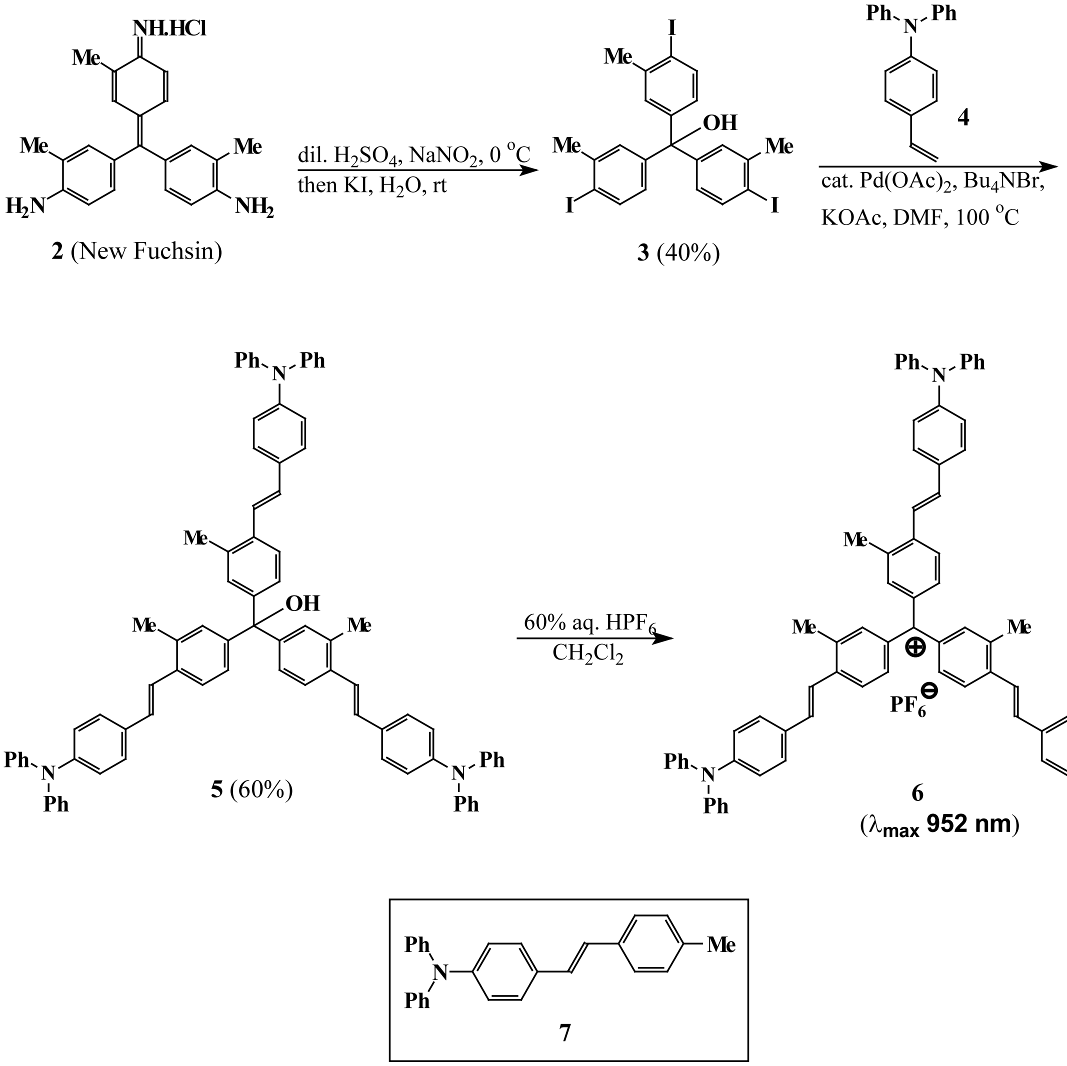


Figure 1. Absorption (left) and emission (right) spectra of **5** in CH_2Cl_2.



Scheme 1.

red shifted from that of the model monochromophore **7** (λ_{max} 366 nm, ε_{max} 2.10×10^4 M^{-1} cm^{-1})[9] indicating a small degree of homoconjugation through the central tetrahedral carbon in **5**. Such homoconjugative effects in centrally tetrahedral molecules was first reported by Bazan et al. for tetrastilbenylmethane[10a,b] and later corroborated by Müller et al. as well as by us for analogous compounds.[9,10c] More significantly, the molar absorptivity of **5** at 378 nm is much greater than three times the value of **7**, indicating constructive excitonic coupling between the three stilbenoid arms in **5**. Such a pronounced hyperchromic effect arises due to the rigid tetrahedral arrangement of the chromophores in **5** which leads to a high degeneracy of the molecular orbitals.[11] It was nonetheless expected, being one of the basic premises of our extended octupolar design. The dye base **5** produced a strong fluorescence with a maximum at 460 nm (λ_{exc} 375 nm) which is also red-shifted from the emission maximum of **7** by ca. 40 nm. Such a large red shift in the emission maximum is probably due to intermolecular associations (excimer formation), especially given the symmetric nature of **5** and its hydrogen bonding prospects. Excimer formation is also evident from the considerable red tailing (up to 600 nm) in the emission spectrum (Fig. 1).

Protonation of **5** in CH_2Cl_2 with a twofold excess of 60% aq. HPF_6 gave a blue violet solution which was dried over anhydrous K_2CO_3. Removal of solvent at room temperature by flushing with nitrogen then gave the NIR dye **6** as a deep violet solid. The dye was freely soluble in polar organic solvents like CH_2Cl_2 or $CHCl_3$. But, in alcoholic solvents, it rapidly lost colour and the NIR band. The absorption spectrum of **6** in MeOH (yellow solution) was identical with that of the dye base **5**. Perhaps, in a methanolic medium, the methoxy analog of **5** is produced via reaction of the central carbocation with MeOH. Although we could not get a correct elemental analysis for the dye due to the presence of residual HPF_6, the ^1H NMR spectrum of **6** clearly indicated the formation of the extended octupolar structure.[12] Thus, the aromatic methyl protons in **6** appeared at δ 2.46, a more downfield position compared to the methyl protons of **5**. Moreover, **6** showed a new three proton doublet (J 8.7 Hz) at 7.93 ppm. The latter, we believe, is due to the 6′-Hs on the aromatic rings that are directly attached to the central carbocation of **6**.[13] The absorption spectrum of **6** produced a maximum at 954 nm with a large molar extinction coefficient (ε_{max} 7.77×10^4 M^{-1} cm^{-1}) (Fig. 2). It may be noted that Crystal Violet **8**, the parent octupolar dye, shows an absorption maximum in the visible region (λ_{max} 590 nm). Compared to Crystal Violet, **6** shows a 360 nm bathochromic shift as a result of our extended octupolar design. Another attractive feature of **6** is its large molar extinction coefficient. This results from two degenerate transitions involving promotion of an electron from the non-bonding molecular orbital (NBMO) to the LUMO. Such a high degree of degeneracy of electronic transitions in cationic triphenylmethane dyes can only be achieved in a trigonally symmetric system and, hence, the advantage of our octupolar design over the conventional linear dipolar strategy (vide supra).

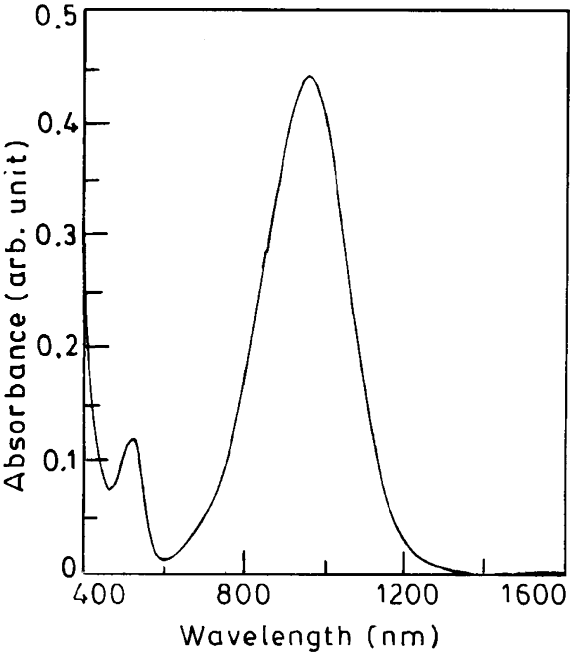
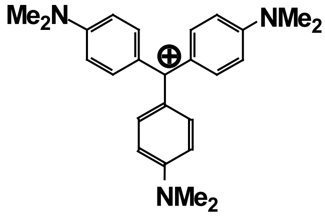


Figure 2. Absorption spectrum of **6** in CH_2Cl_2.

However, we note that the λ_{max} of **6** is more than 100 nm blue shifted compared to the ferrocene based octupolar NIR dye **1** (λ_{max} 1068 nm).[2] Therefore, it appears that metal to ligand charge transfer (MLCT) transitions which were responsible for the NIR absorption in **1** are somewhat superior to NBMO–LUMO interactions in inducing low energy transitions in carbocation ended donor–acceptor systems.



Crystal Violet **8**
(λ_{max} 590 nm)

The choice of the weakly basic triphenylamine (pK_a too small to measure) as the donor was also critical. Analogous systems where N,N-dimethylaniline acts as the donor suffer from concomitant protonation of the anilino nitrogen (pK_a of N,N-dimethylaniline is 4.39) during protonation of the central 3° carbinol.[14] This eventually leads to an equilibrium mixture of the neutral dye and its N-protonated species, the latter predominating. Consequently, charge transfer in such systems is heavily disrupted due to the protonated nature of the nitrogen donors resulting in absorptions in the visible range (λ_{max} ca. 600 nm).

In conclusion, we have described a new organic NIR dye **6** (λ_{max} 954 nm) comprised of a cation centered extended octupole having triphenylamine donors. By virtue of its trigonally symmetric nature, the dye shows a large molar extinction coefficient (log ε 4.9). Based on these design elements, preparation of other octupolar NIR dyes are currently under way.

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7. $Pd(OAc)_2$ (3 mg) was added to a degassed mixture of **3** (0.07 g, 0.10 mmol), 4-vinyltriphenylamine **4** (0.11 g, 0.41 mmol), Bu_4NBr (0.10 mmol, 0.31 mmol) and KOAc (0.075 g, 0.76 mmol) in DMF (5 mL) and the mixture heated at 100°C with vigorous stirring for 36 h. It was then poured into water, extracted with CH_2Cl_2 and the solvent removed under reduced pressure. Purification of the residue, first by column chromatography over silica gel (40% CH_2Cl_2 in light petroleum) followed by preparative thin layer chromatography over silica gel (50% CH_2Cl_2 in light petroleum) gave **5** (0.066 g, 60%); UV–vis [CH_2Cl_2, λ in nm (log ε)] 232 (4.67), 302 (4.70), 374 (4.85); IR (KBr, cm^{-1}) 3400 (w), 1589 (s), 1508 (s), 1490 (s), 1328 (s), 1313 (m), 1278 (m); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 2.39 (s, 9H), 6.95 (d, 3H, *J* 16.2 Hz), 7.00–7.12 (m, 27H), 7.18 (s, 3H), 7.22–7.28 (m, 12H), 7.39 (d, 6H, *J* 8.7 Hz), 7.52 (d, 6H, *J* 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 82.0, 123.4, 124.0, 124.8, 124.9, 125.0, 126.3, 127.8, 129.6, 129.9, 130.1, 132.2, 135.6, 135.9, 146.1, 147.7, 147.9.
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